Supporting of

Effects of OH radical and SO_2 concentrations on photochemical reactions of mixed anthropogenic organic gases

Junling Li et al.

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Offline measurement: ESI-Q-ToF-MS

The extracted solutions were analyzed with electrospray ionization quadrupole time-of flight mass spectrometry (ESI-Q-ToF-MS, Bruker Compact). Positive ion mode was used for the ESI-Q-ToF-MS. In general, the theoretical molecular mass of a compound refers to the monoisotopic mass of the compound, which is the sum of the masses of its constituent elements, with each element mass choosing the mass of its most abundant isotope. The expected elemental formula means the formula with the theoretical molecular mass. The molecular mass of measured elemental formula is usually not the sum of masses of the most abundant isotopes of each element. Thus, mass accuracy (ppm) is applied to indicate the difference degree between the measured and the theoretical molecular mass of the elemental formula. The mass resolution of this used instrument is ＞20000.

Table S1. Initial conditions and general results of the NO experiments conducted in this work.

Number	Date	Initial conditions									General Results		
		1,3,5-TMB (ppb)	n-dodecane (ppb)	SO_2 (ppb)	NO (ppb)	NO_2 (ppb)	NO_X (ppb)	ppbC/ppb	$J(NO_2)$ ($\times 10^{-3}$ s^{-1})	T (°C)[a]	O_3 (ppb)[b]	M[c] (μg/m^3)	Mo corr. (μg/m^3)[d]
L-NO-Mix-1	2020.1110	177.8	29.2	6.6	212	13	225	8.67	3.7	29	267	8.4	27.5
L-NO-Mix-2	2020.1227	192.4	26.4	8.1	336	18	354	5.79	2.3	20	71	14.2	58.8
H-NO-Mix-1	2020.1231	185.8	25.7	25.5	335	20	355	5.58	3.2	18	138	59	70.3
H-NO-Mix-2	2020.1214	176.6	23.2	33	323	24	347	5.38	2.9	15	97	60.6	72.4
H-NO-Mix-3	2020.1113	188.4	29.9	105	228	14	242	8.49	3.1	28	252	169	185.3
L-NO-TMB-1	2020.1225	190.2	--	9.4	326	22	348	4.92	2.6	23	123	6	24.7
L-NO-TMB-2	2021.0102	191.7	--	9.5	321	23	344	5.02	2.1	15	81	16.7	31.7
H-NO-TMB-1	2020.1216	182.8	--	32	314	33	347	4.74	3.2	20	186	39.8	49.1
H-NO-TMB-2	2021.0105	190.1	--	35	313	45	358	4.78	2.9	16	100	52.4	63.3
L-NO-Dod-1	2020.1221	--	22.9	6.1	309	29	338	0.81	2.5	21	1	6.2	21.1
L-NO-Dod-2	2021.0117	--	29.8	6.4	333	25	358	1.00	2.8	19	0.9	11.6	27.2
H-NO-Dod-1	2020.1219	--	27.3	33	310	27	337	0.97	2.5	19	1.2	8.1	19.9
H-NO-Dod-2	2021.0112	--	23	71	355	38	393	0.70	2.4	18	1.2	5.2	22.1

a: the temperature here is the value at noon; b: the ozone concentration here is the highest value of the reaction process; c： M here is the mass concentration of formed secondary aerosol; d: the mass concentration here is corrected after taking both vapor and particle wall loss into account.

Table S2. Initial conditions and general results of the HONO experiments conducted in this work.

Number	Date	Initial conditions									General Results		
		1,3,5-TMB (ppb)	n-dodecane (ppb)	SO_2 (ppb)	NO (ppb)	NO_2 (ppb)	NO_X (ppb)	ppbC/ppb	$J(NO_2)$ ($\times 10^{-3}$ s^{-1})	T (°C)[a]	O_3 (ppb)[b]	M[c] (μg/m^3)	Mo corr. (μg/m^3)[c]
L-HONO-Mix-1	2020.1127	137.9	23.9	4	106	298	404	3.78	3.4	21	243	20.3	23.1
L-HONO-Mix-2	2020.1208	185.9	23.2	5	108	261	369	5.29	3.1	19	231	35.7	47.6
H-HONO-Mix-1	2020.1120	193.1	27.1	23.6	159	286	445	4.64	3.9	27	317	304.5	328.3
H-HONO-Mix-2	2020.1123	159.4	23.2	30	96	264	360	4.76	3.6	24	260	368.6	395.8
H-HONO-Mix-3	2021.0622	165.9	28.9	35	43	272	315	5.84	4.3	41	645	340.9	364.8
H-HONO-Mix-4	2021.0120	191.4	26.2	65	130	250	380	5.36	1.9	16	184	534.4	569.4
L-HONO-TMB-1	2020.1210	196	--	3.6	117	296	413	4.27	2.5	22	231	12.3	35.2
L-HONO-TMB-2	2021.0124	216.9	--	0	105	236	341	5.72	1.2	15	148	30.5	40.9
H-HONO-TMB-1	2020.1125	179.1	--	28	85	265	350	4.61	3.4	24	212	240.1	261.4

H-HONO-TMB-2	2021.0126	157.4	--	31	113	230	343	4.13	3.2	24	225	176.7	194.9
L-HONO-Dod-1	2021.0131	--	24.4	3	116	227	343	0.85	2.2	16	5	19	29.6
H-HONO-Dod-1	2021.0129	--	24.9	27	104	235	339	0.88	3.2	19	7	173.8	189.5
H-HONO-Dod-2	2020.1203	--	24.7	35	116	313	429	0.69	3.4	21	5	123.5	137.2

a: the temperature here is the value at noon; b: the ozone concentration here is the highest value of the reaction process; c: M here is the mass concentration of formed secondary aerosol; d: the mass concentration here is corrected after taking both vapor and particle wall loss into account.

Table S3. List of functional groups in SOA extracts.

Functional groups	**Wavenumber (cm^{-1})**
C-OH in alcohol	3360
O-H stretching vibration of hydroxyl and carboxyl groups	3100-3300 (3192)
C-H stretching vibration in aromatics	3000-3200
CH_3 stretching vibration in alkanes	2960
CH_2 stretching vibration in alkanes	2921, 2850
C=O stretching vibrations of ketones, aldehydes, and carboxylic acids	1660, 1633
deformation vibrations of methyl and methylene groups	1465, 1415
$-ONO_2$ stretching in nitrate ester	1268
the absorption peak of sulfate	1000-1200
sulfate group in sulfate and organic compounds	1100
absorption band of S=O in organic compound	1040-1070

Table S4. Identified mass spectral peaks, molecular formulas, molecular weights, and accuracy of mixed experiments-derived SOA.

Molecular formula	M+H	M+Na	M-H	H-HONO-MIX	L-HONO-MIX	H-NO-MIX	L-NO-MIX	Accuracy (ppm)	RDB[a]
$C_4H_{10}O_3$			105.0549	√				-2.56	0
$C_5H_6O_3$			113.02286	√				-8.93	3
$C_7H_6O_2$			121.0283	√	√			-5.41	5
$C_5H_8O_4$			131.03438		√			-0.41	2
$C_9H_{12}O_2$			135.08076	√		√	√	-1.70	4
$C_4H_{10}O_3S$			137.02873				√	9.98	0
$C_7H_{12}O_3$			143.07068		√			-0.97	2
$C_8H_{16}O_2$			143.10798	√				5.42	1

$C_6H_{10}O_4$			145.05036		√			1.90	2
$C_5H_8O_3S$			147.01289			√		8.84	2
$C_4H_6O_6$			149.00867	√				0.38	2
$C_5H_{10}O_3S$			149.02814		√			6.04	1
$C_9H_{18}O_2$			157.12184	√				-6.46	1
$C_6H_8O_3S$			159.01119	√	√			-2.52	3
$C_7H_6O_3$		161.02144				√	√	-0.14	5
$C_5H_{10}O_6$			165.03948	√	√		√	-2.62	1
$C_6H_{12}O_6$			179.05436	√	√	√	√	-6.72	1
$C_5H_{10}O_7$			181.03567				√	0.84	1
$C_5H_8O_7$	181.0352			√	√	√	√	2.06	2
$C_{12}H_{22}O$	183.17437			√	√	√	√	-2.84	2
$C_7H_8O_4S$			187.00505			√		-7.78	4
$C_6H_{12}O_7$			195.05121				√	3.75	1
$C_8H_7NO_5$			196.02295	√	√	√	√	-8.40	6
$C_7H_{10}O_5S$			205.01678		√	√		-1.41	3
$C_9H_{14}O_4$		209.08031			√			6.37	3
$C_{14}H_{20}O_2$	221.15394			√	√		√	-0.97	5
$C_7H_{12}O_6S$			223.02585		√		√	-8.00	2
$C_7H_{10}O_8$	223.04424				√			-5.17	3
$C_{14}H_{24}O_2$	225.1834				√			-9.13	3
$C_{14}H_{28}O_2$			227.20095	√	√		√	-0.68	1
$C_{10}H_{16}O_6$	233.10277				√			1.10	3
$C_{12}H_{26}O_4$			233.07539		√	√	√	0.45	0
$C_{13}H_{24}O_2$		235.16615			√			-5.31	2
$C_{11}H_{12}O_6$			239.05639	√	√		√	3.46	6
$C_8H_{10}O_7$		241.03098					√	-5.98	4
$C_{12}H_{14}O_6$			253.07162	√	√		√	1.61	6
$C_{15}H_{31}NO_2$			256.22589	√	√	√		-6.89	1
$C_6H_{12}O_{11}$	261.04745						√	6.37	1
$C_{15}H_{22}O_4$	267.16029			√	√	√		2.45	5
$C_{17}H_{34}O_2$			269.24882	√				2.84	1
$C_{12}H_{14}O_7$	271.0823			√		√		1.93	6
$C_{14}H_{12}O_6$	277.07058					√		-2.29	9
$C_{14}H_{21}NO_5$	282.13525			√	√			3.91	6
$C_{14}H_{23}NO_5$	284.15113			√	√			4.69	5
$C_{17}H_{35}NO_2$			284.26063	√		√		5.89	1
$C_{14}H_{25}NO_5$	286.15679			√	√	√		1.58	4
$C_{12}H_{10}O_7$		289.03457			√			7.43	8
$C_{17}H_{34}O_2$		293.24635		√	√			2.39	1
$C_{14}H_{30}O_4S$			293.1798	√	√	√	√	3.90	0
$C_{19}H_{38}O_2$			297.27787	√	√			-5.00	1
$C_{14}H_{21}NO_6$	298.13009			√	√	√		3.45	6
$C_{18}H_{36}O_3$			299.25831	√				-1.04	1
$C_{17}H_{34}O_4$			301.23624	√	√			-1.00	1
$C_{18}H_{28}O_4$	309.20768			√		√	√	3.54	5
$C_{17}H_{28}O_3S$			311.16817	√	√	√	√	0.25	4
$C_{20}H_{24}O_3$	313.18112			√			√	2.40	9
$C_{10}H_{18}O_{11}$			313.07845	√	√		√	4.36	2
$C_{12}H_{22}O_8$		317.12123		√			√	-0.02	2

$C_{11}H_{10}O_{11}$			317.01445			√		-0.11	7
$C_{19}H_{28}O_2$		321.27759		√	√			1.99	1
$C_{19}H_{32}O_4$			323.22062				√	-4.99	4
$C_{21}H_{26}O_3$			325.18201	√	√	√	√	5.04	9
$C_{19}H_{38}O_4$			329.26913	√	√	√	√	-0.17	1
$C_{17}H_{24}O_5$		331.15274		√			√	1.80	6
$C_{17}H_{28}O_5$		335.18129		√	√			-6.42	4
$C_{15}H_{24}O_7$		339.14059					√	-4.08	4
$C_{19}H_{32}O_3S$			339.20067	√	√	√	√	3.77	4
$C_{21}H_{42}O_3$			341.30626	√				0.69	1
$C_{21}H_{42}O_2$		349.30879			√			1.55	1
$C_{21}H_{36}O_4$			351.2518				√	-4.94	4
$C_{23}H_{30}O_3$			353.21004	√			√	-4.61	9
$C_{18}H_{32}O_6S$			375.18653	√	√			2.40	3
$C_{25}H_{34}O_3$			381.24039	√			√	-2.58	9
$C_{21}H_{42}O_4$		381.29843				√		0.92	1
$C_{12}H_{18}O_{14}$			385.06093			√		-2.37	4
$C_{20}H_{20}O_8$			387.10571	√				-5.90	11
$C_{10}H_{16}O_{14}S$			391.0178			√		-1.15	3
$C_{24}H_{35}NO_4$	402.26369			√	√			-1.85	8
$C_{20}H_{36}O_6S$			403.21776	√	√		√	2.32	3
$C_{25}H_{28}O_3S$			407.16857			√		1.18	12
$C_{25}H_{42}O_3S$			421.27961	√				4.67	5
$C_{24}H_{40}O_6$	425.29015				√			-0.39	5
$C_{16}H_{20}O_{14}S$			467.05113		√			3.38	7
$C_{26}H_{44}O_7$	469.31634				√			-0.40	5
$C_{30}H_{60}O_4$			483.4415	√				0.34	1
$C_{24}H_{36}O_{10}$	485.23785			√				-1.69	7
$C_{27}H_{50}O_6$		493.35116		√				1.32	3
$C_{32}H_{64}O_4$			511.47436		√		√	3.37	1
$C_{26}H_{41}NO_9$	512.28878			√				5.51	7
$C_{23}H_{22}O_{12}S$			521.07702			√		3.16	13
$C_{34}H_{62}O_4$			533.45851	√			√	2.86	4
$C_{34}H_{66}O_4$			537.48731	√				-1.82	2
$C_{34}H_{68}O_4$			539.50358				√	-0.66	1
$C_{33}H_{67}NO_4$			540.49708		√			1.07	2
$C_{34}H_{44}O_8$	545.31236			√				1.68	10
$C_{29}H_{44}O_0$		559.28929		√				1.77	8
$C_{36}H_{72}O_4$			567.5355		√			-0.41	1
$C_{36}H_{74}O_4$			569.55075	√				-0.24	0
$C_{37}H_{74}O_6$			613.53995				√	-1.25	1

a: RDB is the abbreviation of ring and double-bond equivalent.

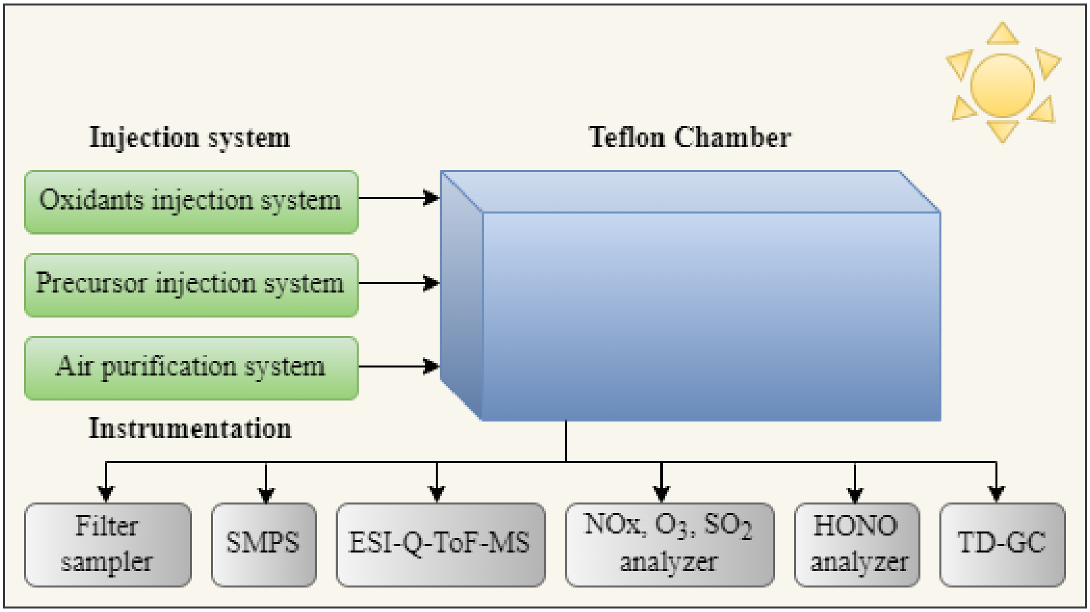
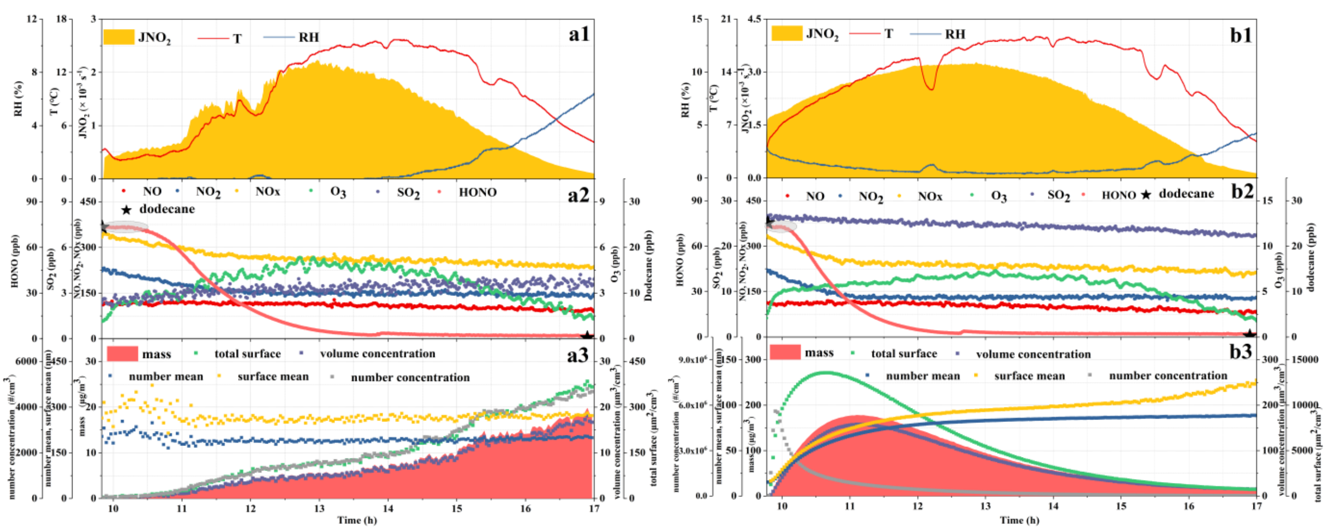


Figure S1. Schematic of the CRAES smog chamber.



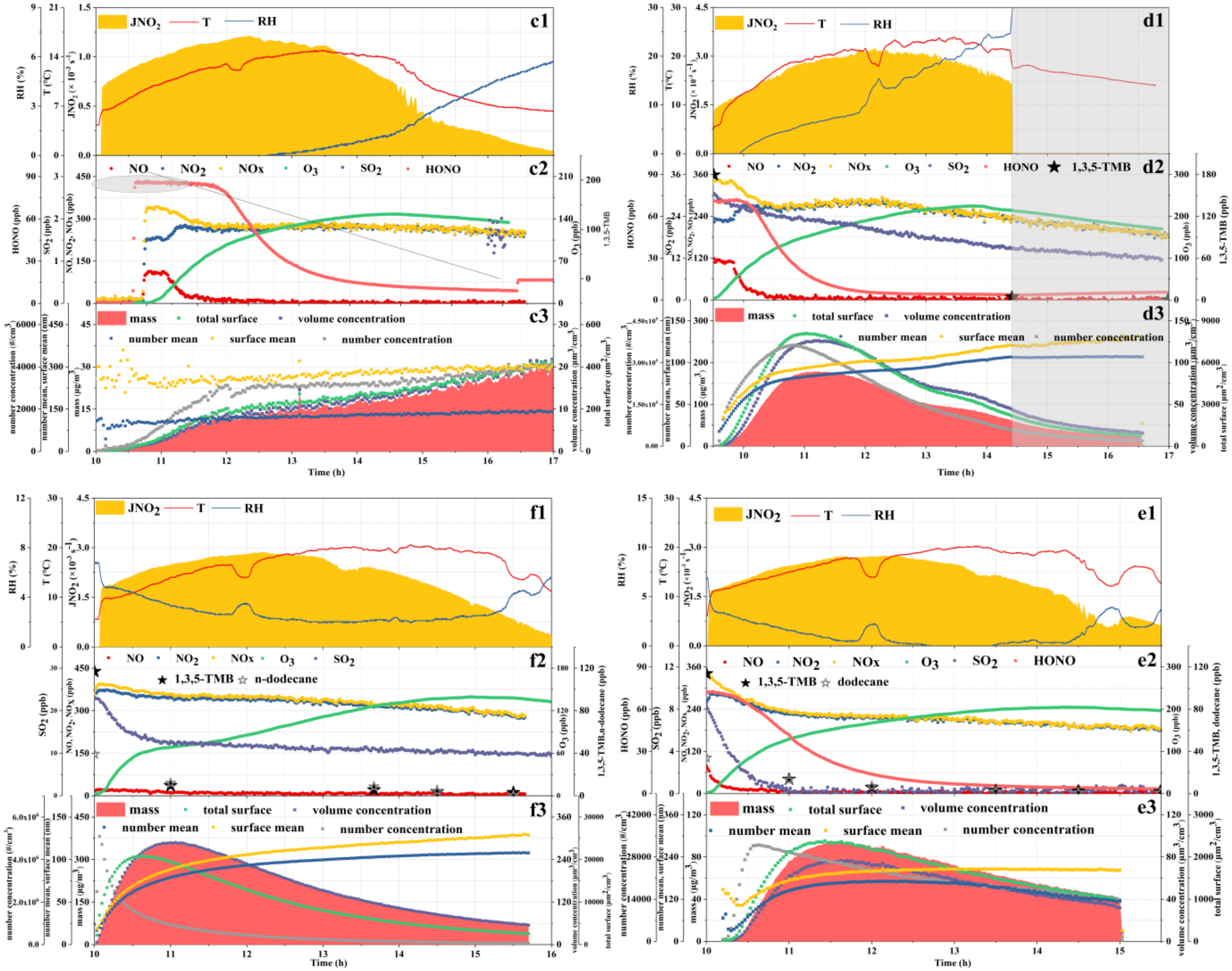
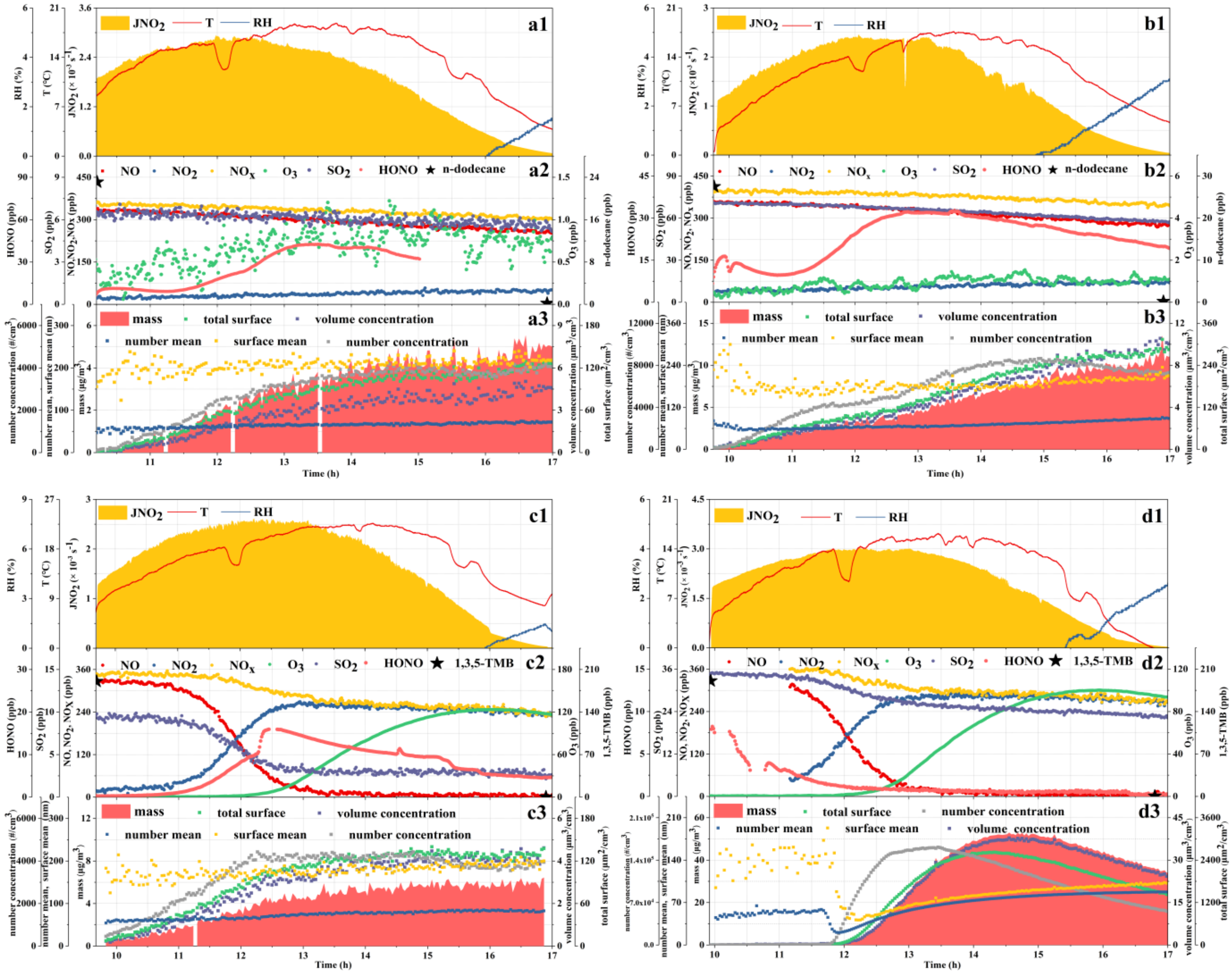


Figure S2. Reaction profiles of the HONO experiments: (a) n-dodecane + HONO + low concentration SO_2 (L-HONO-Dod); (b) n-dodecane + HONO + high concentration SO_2 (H-HONO-Dod); (c) 1,3,5-trimethylbeneze + HONO + low concentration SO_2 (L-HONO-TMB); (d) 1,3,5-trimethylbeneze + HONO + high concentration SO_2 (H-HONO-TMB); (e) n-dodecane + 1,3,5-trimethylbeneze + HONO + low concentration SO_2 (L-HONO-Mix); (f) n-dodecane + 1,3,5-trimethylbeneze + HONO + high concentration SO_2 (H-HONO-Mix).


a1
JNO2 T RH
a2
NO NO2 NOx O3 SO2 HONO n-dodecane
a3
mass total surface volume concentration
number mean surface mean number concentration
b1
JNO2 T RH
b2
NO NO2 NOx O3 SO2 HONO n-dodecane
b3
mass total surface volume concentration
number mean surface mean number concentration
c1
JNO2 T RH
c2
NO NO2 NOx O3 SO2 HONO 1,3,5-TMB
c3
mass total surface volume concentration
number mean surface mean number concentration
d1
JNO2 T RH
d2
NO NO2 NOx O3 SO2 HONO 1,3,5-TMB
d3
mass total surface number concentration
number mean surface mean volume concentration
Time (h)

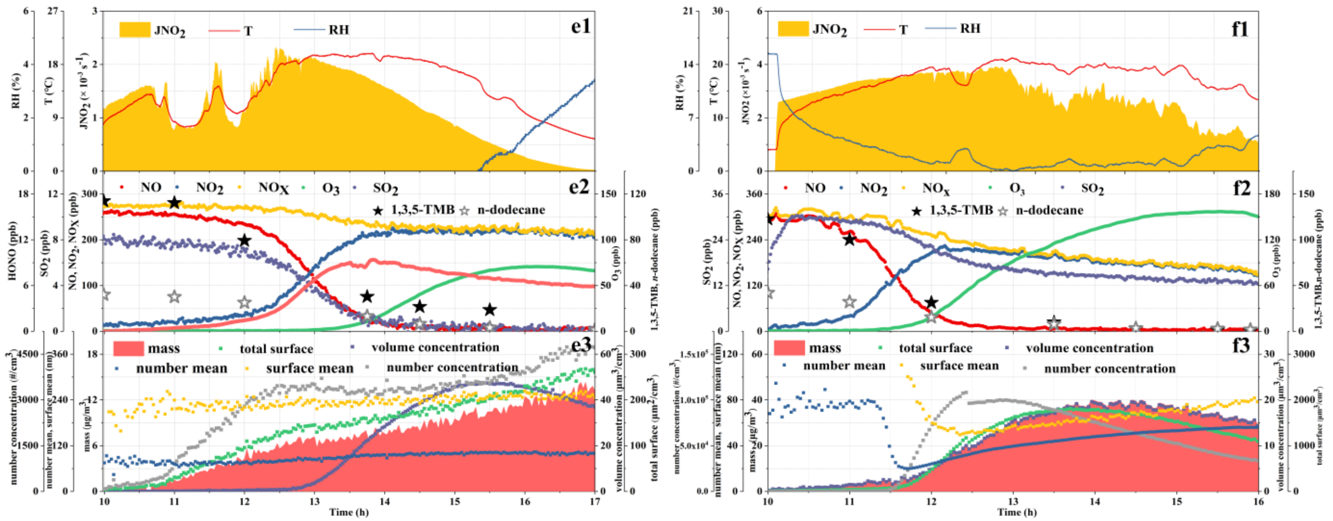


Figure S3. Reaction profiles of the NO experiments: (a) *n*-dodecane + NO + low concentration SO_2 (L-NO-Dod); (b) *n*-dodecane + NO + high concentration SO_2 (H-NO-Dod); (c) 1,3,5-trimethylbeneze + NO + low concentration SO_2 (L-NO-TMB); (d) 1,3,5-trimethylbeneze + NO + high concentration SO_2 (H-NO-TMB); (e) *n*-dodecane + 1,3,5-trimethylbeneze + NO + low concentration SO_2 (L-NO-Mix); (f) *n*-dodecane + 1,3,5-trimethylbeneze + NO + high concentration SO_2 (H-NO-Mix).

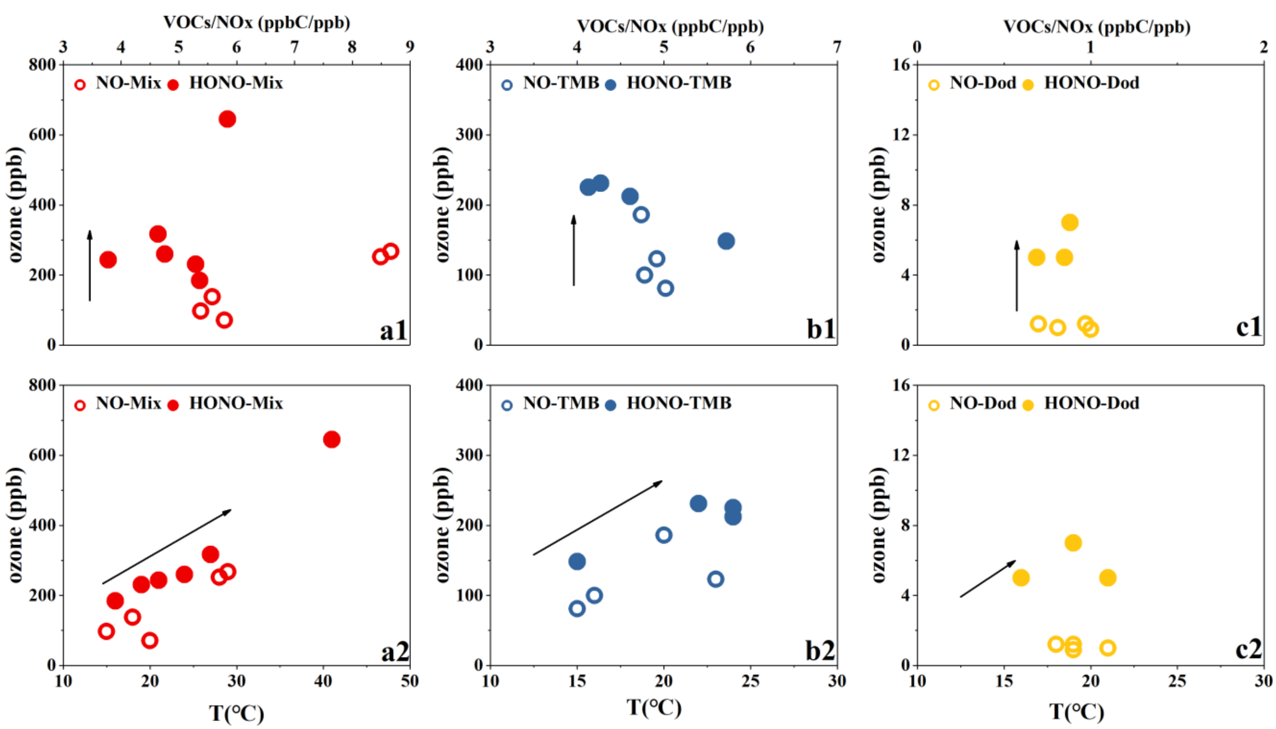


Figure S4. Ozone formation in the NO and HONO experiments. The temperature (T) and ozone concentration here refers to the maximum value during the reaction process.

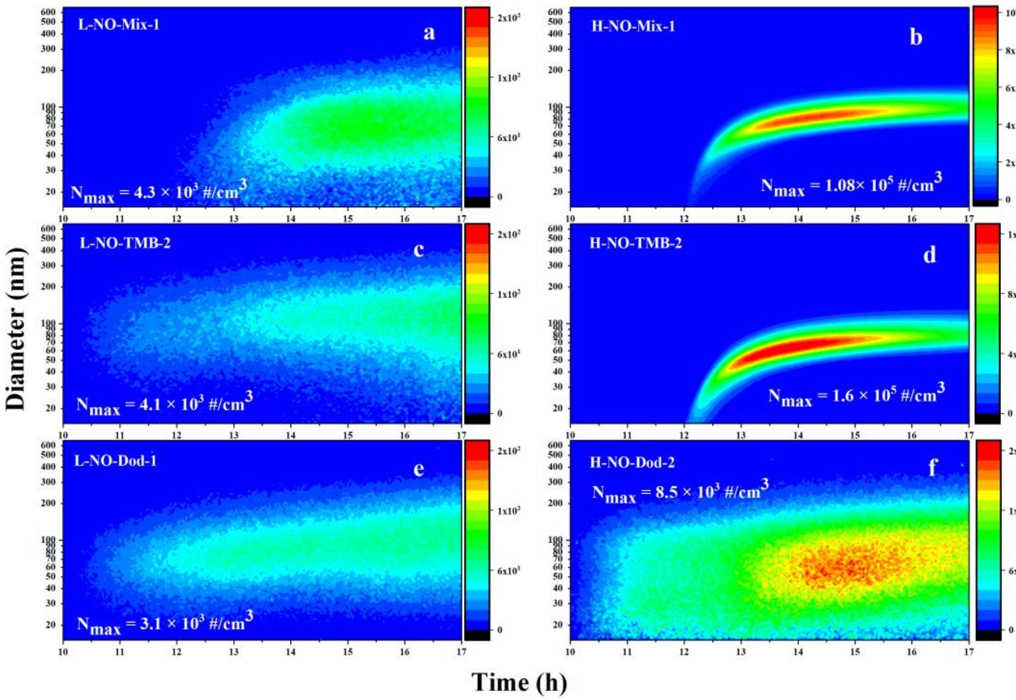


Figure S5. Number concentration of particles formed under NO conditions. (a) mixture-NO experiment with low SO_2 concentration, L-NO-Mix; (b) mixture-NO experiment with high SO_2 concentration, H-NO-Mix; (c) 1,3,5-TMB-NO experiment with low SO_2 concentration, L-NO-TMB; (d) 1,3,5-TMB-NO experiment with high SO_2 concentration, H-NO-TMB; (e) *n*-dodecane-NO experiment with low SO_2 concentration, L-NO-Dod; (f) *n*-dodecane-NO experiment with high SO_2 concentration, H-NO-Dod. The color bar in the figure is in the unit of #/cm³. See Table S1 for the experimental conditions.

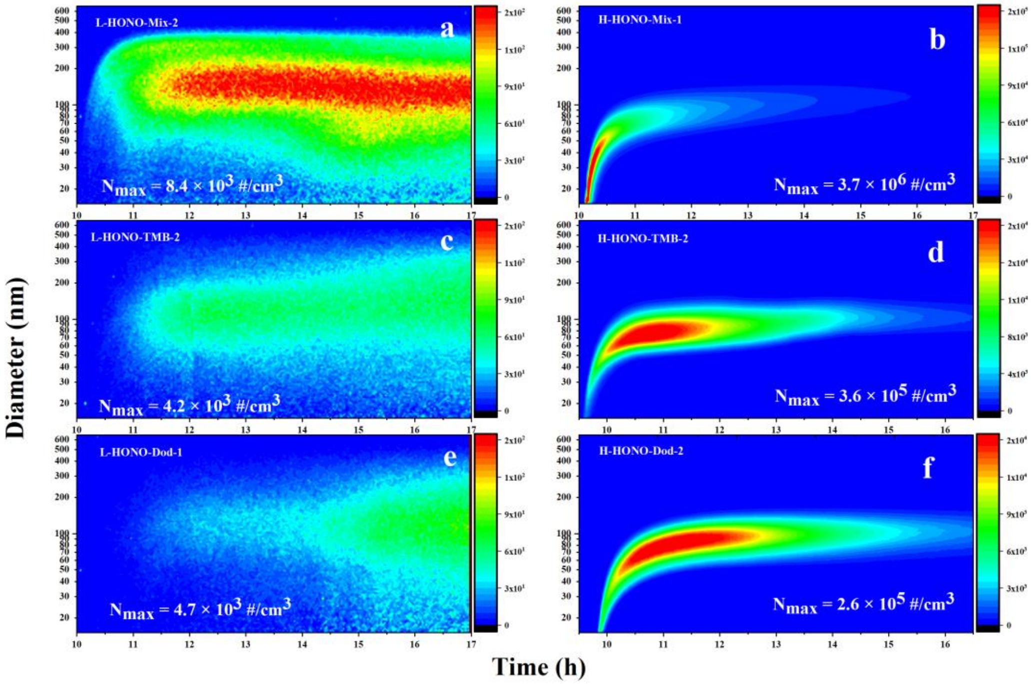


Figure S6. Number concentration of SA formed under HONO conditions. (a) mixture-HONO experiment with low SO_2 concentration, L-HONO-Mix; (b) mixture-HONO experiment with high SO_2 concentration, H-HONO-Mix; (c) 1,3,5-TMB-HONO experiment with low SO_2 concentration, L-HONO-TMB; (d) 1,3,5-TMB-HONO experiment with high SO_2 concentration, H-HONO-TMB; (e) *n*-dodecane-HONO experiment with low SO_2 concentration, L-HONO-Dod; (f) *n*-dodecane-HONO experiment with high SO_2 concentration, H-HONO-Dod. The color bar in the figure is in the unit of #/cm^3. See Table S2 for the experimental conditions.

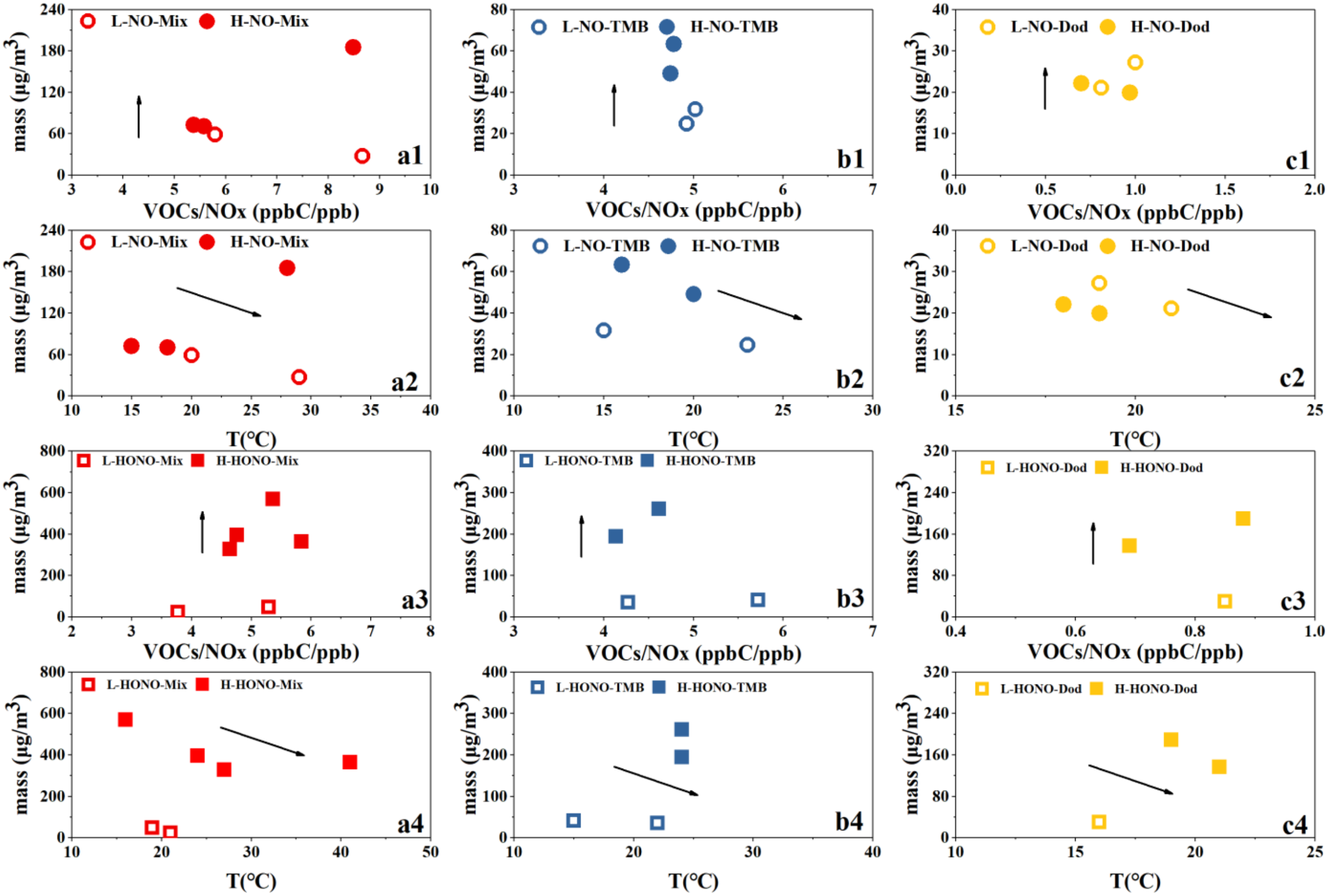


Figure S7. Particle formation of NO and HONO experiments. The temperature (T) and particle mass concentration here refers to the maximum value during the reaction process.

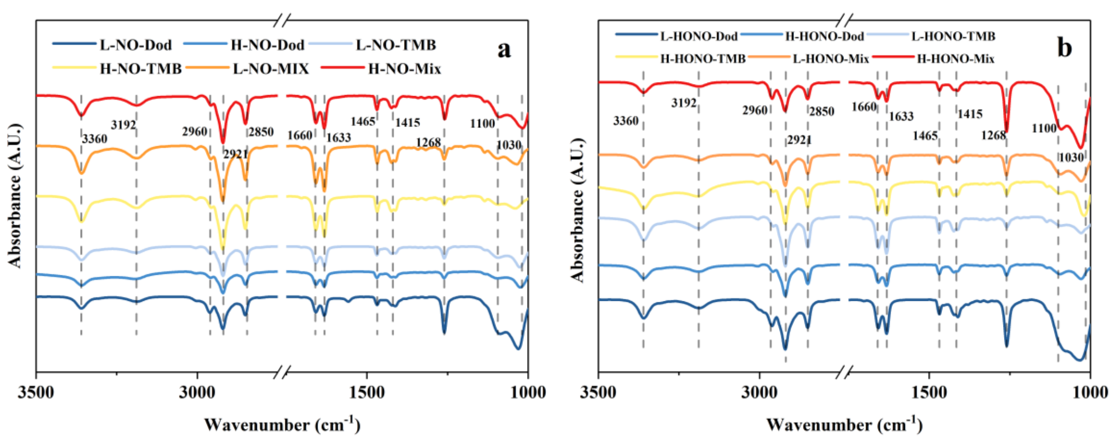


Figure S8. Infrared spectra (IR) of aerosols under (a) NO conditions and (b) HONO conditions.